

# Preceramic Polymer Blends as Novel Environmentally Safe Fire Retardants

## Inventors:

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## 1. Abstract

This patent describes the use of preceramic inorganic and organometallic polymers as additives and in blends with organic polymers for reducing flammability, i.e., as a fire retardant (FR) for commodity and engineering polymers.

## 2. Description

Current fire retardants have a number of problems depending on the system. Halogen based fire retardants (which may produce toxic and corrosive combustion products) and phosphorus based fire retardants increase the amount of carbon monoxide and smoke during combustion (by five to ten times), hydrates (e.g. ATH, aluminum trihydrate) which decompose by an endothermic process to produce water, must be used at such high loadings that (40-70% wt) the physical properties of the base polymer are excessively compromised. New fire retardants are needed that do not have these shortcomings. This is especially important for US companies trying to sell products in Europe, where a negative public opinion exists towards halogen base fire retardants, and a new European environmental law, the "eco-labeling" law, has passed which requires a label on all products that describes the materials used in the product. These issues are forcing companies to look for new, environmentally acceptable fire retardants for their FR polymer products.

The use of preceramic inorganic, hybrid (organic-inorganic) and organometallic polymers as additives and in blends with organic polymers reduces polymer flammability without any of the above problems. Typical preceramic polymers such as polysilsesquioxane (PSS) resins and polycarbosilane copolymers (PCS) were blended with common organic polymers such as polypropylene, Kraton™ (polystyrene-polybutadiene-polystyrene, SBS) and Pebax™ (polytetramethylene ether-nylon copolymer). The typical Pebax™ blends exhibit 50% to 70% lower peak heat release rate (HRR) than pure Pebax™ without significantly increasing the smoke or carbon monoxide levels during the combustion. HRR has been shown to be the most important parameter to consider for evaluation of the Fire-Safety of materials (Babrisk). The HRR data for the Pebax™ and the Pebax™ blends is shown in Figure 1.

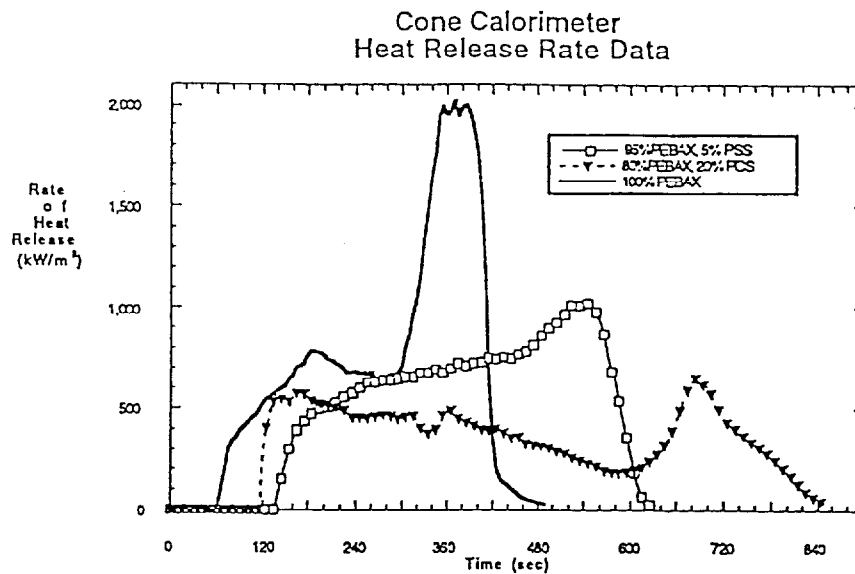


Fig. 1. Heat release rate (HRR) data for Pebax, a Pebax/20% PCS blend and Pebax/5% PSS blend.

This data shows a 50% to 70% reduction in the maximum peak HRR and a 100% increase in the ignition time for the blends. The HRR data for polypropylene and polypropylene blended with PSS is shown in Figure 2 and the HRR data for Kraton, Kraton blended with PCS and PSS respectively, shown in Figure 3, reveal similar flammability performance advantages using this new FR approach.

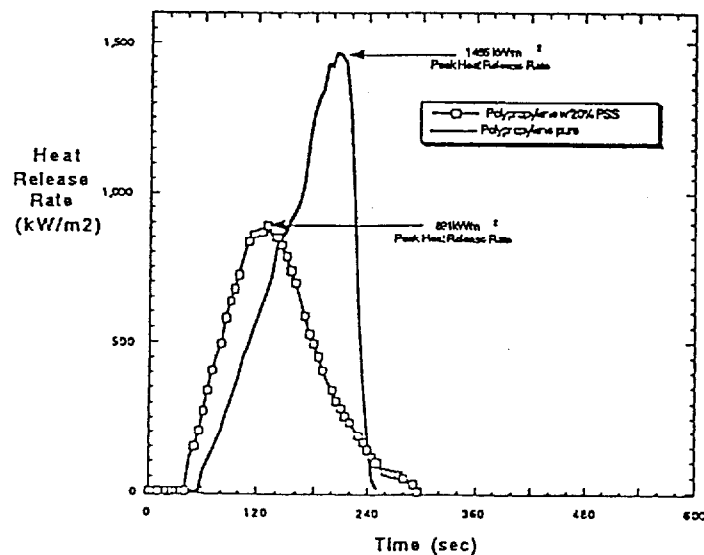


Fig. 2. Heat release rate (HRR) data for Polypropylene and a Polypropylene / 20% PSS blend.

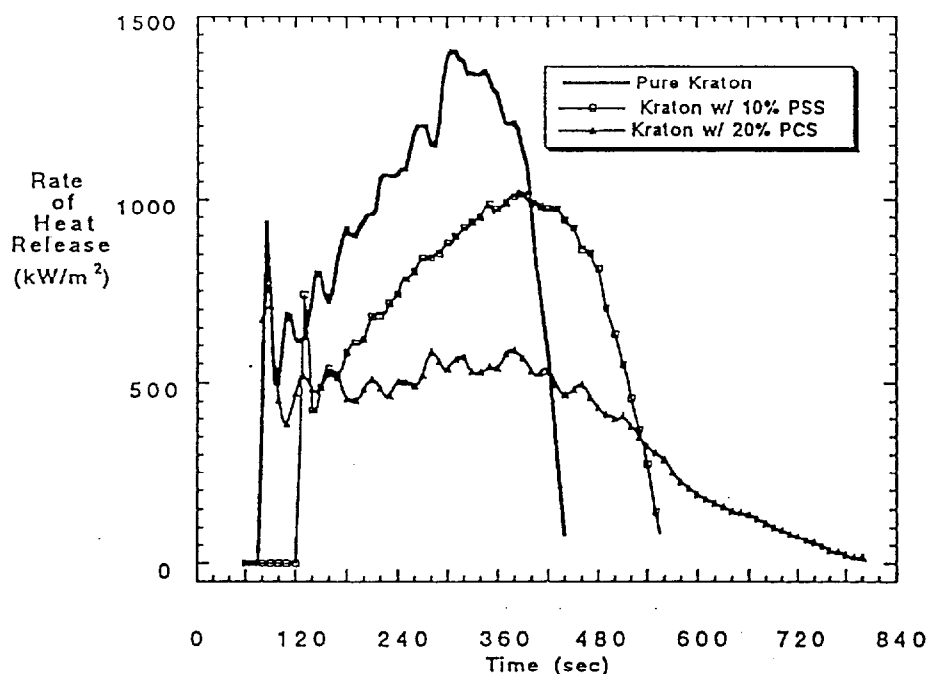


Fig. 3. Heat release rate (HRR) data for Kraton, Kraton / 10% PSS blend and Kraton / 20% PCS blend. This data shows a 30% to 40% reduction in the peak HRR for the blends.

This data shows a 40% reduction in the peak HRR for the blend. Table 1 shows a more complete set of combustion data for these systems. These blends do not produce toxic compounds such as dioxins and dibenzofurans during the burning as some halogen base fire retardants are alleged to. They also do not increase the amount of carbon monoxide or smoke during the combustion.

The data in Table 2 show that the blending of the preceramic polymers can also be used to tailor the mechanical properties of commercial resins. For example the moduli and char yield of these polymer blends can be selectively controlled over a wide range. An additional improvement derived from these systems is that the melt viscosity of the mixtures is higher than that of the pure polymers due to the high melt viscosity of the preceramic polymers. The melt viscosity effect combined with the encapsulating effect of the ceramic char, formed during the burning, reduces dripping during flammability tests such as UL 94 and improves the flammability rating. Furthermore the high melt viscosity increases the thickness and therefore the performance of the char layer that forms as the preceramic decomposes.

Table 1. Cone Combustion Data for Polymers and Preceramic Polymer-Polymer Blends.

Sample	Char Yield (%)	Peak HRR ( $\Delta\%$ ) (kW/m <sup>2</sup> )	Mean HRR ( $\Delta\%$ ) (kW/m <sup>2</sup> )	Mean Heat of Combustion (MJ/kg)	Total Heat Released (MJ/m <sup>2</sup> )	Mean Ext. Area (m <sup>2</sup> /kg)	Mean CO yield (kg/kg)
PP	0	1,466	741	34.7	141	650	0.03
PP w/ 20%PSS	17	892 (40%)	432 (42%)	29.8	106	821	0.03
PEBAX™	0	2,020	780	29.0	332	187	0.02
PEBAX™ w/ 20%PCS	15	699 (65%)	419 (46%)	28.5	272	260	0.02
PEBAX™ w/ 10%PSS	6	578 (72%)	437 (44%)	25.2	301	367	0.02
Kraton™	1	1,405	976	29.3	351	1,750	0.08
Kraton™ w/ 20% PCS	20	825 (42%)	362 (63%)	26.4	266	1,548	0.07
Kraton™ w/ 10% PSS	6	1,027 (27%)	755 (23%)	26.9	324	1,491	0.07

These new fire retardants can be used with commodity and engineering polymers in any application where a fire retarded polymer is required, i.e., carpeting, adhesives, wire and cable insulation and jacketing, fabrics, furniture, structural plastics, chassis, housings etc.

### 2.1. Supplemental Description of the Invention:

Our approach toward developing fire-safe thermoplastic hybrid materials takes advantage of the char forming properties and thermal properties of available preceramic materials (Figure 4) (e.g. polycarbosilanes (PCS), polysilanes (PS), polysilsesquioxane (PSS) resins, polyhedral oligomeric silsesquioxane (POSS) monomers, polymers and copolymers). In such formula R = H, hydrocarbons, substituted hydrocarbons R-X, Aromatics Ar, and substituted aromatics Ar-X where X = halogen, phosphorus or nitrogen containing groups. The incorporation of halogen or other inorganic groups such as phosphates and amines directly onto these polymers may additionally afford a "dual" fire-retardancy. Dual fire-retardancy could be achieved by the substituent group controlling the gas-phase combustion chemistry and or contributing to the formation of char and hence controlling the solid-state chemistry.

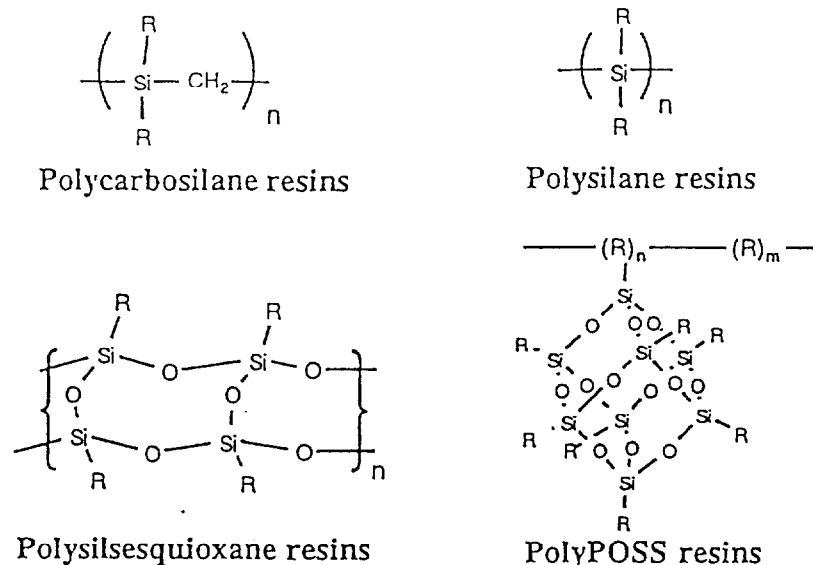


Fig 4. Formula representative of the type of blendable preceramic polymer resins.

The mechanical properties of preceramic polymers are generally not sufficient to allow their application as engineering plastics. However, these preceramic materials can be blended in various proportions with thermoplastics such as polypropylene (or other polyolefins or nylons, polyethers, polyesters) and thermoplastic elastomers such as PEBAX™ (a polyether block polyamide rubber) or Kraton™ (a styrene-butadiene-styrene triblock polymer). The resulting "preceramic polymer-organic polymer" blends have been shown to possess mechanical properties desirable for many engineering applications along with enhanced resistance to combustion and low heat release upon combustion. As shown in the Table 2 the mechanical properties (tensile strength, elongation, Youngs modulus) of the resulting polymer blends can be tailored over a wide range and are dependent upon the percentage of the preceramic incorporated. The thermal properties (such as melt and glass transitions) of the resulting blends are similarly controlled through the percentage of preceramic polymer incorporated into the blend composition. Control over the thermal properties of plastics is desirable for enabling the material to be amenable to a variety of plastic fabrication processes (such as compression molding, extrusion, injection molding, and spraying technologies). The flammability properties (such as ignition time, and HRR) of the resulting blends are similarly controlled through the percentage of preceramic polymer incorporated. Therefore the amount of flame retardancy required for a particular application can easily be selected. An additional benefit of this approach is that since such a wide variety of structures exist for preceramic polymers that an optimal match can be achieved between the preceramic polymer and the organic polymer, allowing optimization of performance for a particular organic polymer. For example PCS appears to be the best preceramic to use for controlling the flammability of nonpolar polymers like Pebax without sacrificing the desirable

range of mechanical properties. In a more polar type organic polymer a preceramic, such as a PSS, with the appropriate level of silanol groups would make a stable high quality blend through favorable (compatibilizing) hydrogen bonding interactions.

The process of blending preceramic polymers with organic polymers enables control over the amount of char formed during combustion. It is the formation of this char that is the key to the FR of these polymer blends. Char formation reduces the amount of small volatile polymer pyrolysis fragments, or fuel, available for burning in the gas phase; this, in turn reduces the amount of heat released and feedback to the polymer surface. The char accomplishes this by insulating the underlying virgin polymer from the external combustion radiation, and/or by trapping decomposition products in it's matrix. It may also re-radiate energy away from the polymer. The physical structure of the char is important in these roles. Foamy char structure appears to be more fire resistant than brittle, thin char. This char enhancing approach is most successful when the polymer chars rapidly and early in the burning process (Kashiwagi). To be useful the charring process must be designed so that it occurs subsequent to the processing temperature and early in the decomposition of the polymer, i.e.,  $T_{\text{processing}} \ll T_{\text{charring}} \sim T_{\text{dec}}$ . Additives that increase the amount of charcoal-like residue or carbonaceous char that forms during polymer combustion are known to be very effective fire retardants.(Weil)

In added support that control over char formation can be achieved via blending preceramic and organic polymers, Figure 4 shows that the amount of char formed during pyrolysis increases as the proportion of preceramic polymer blended with the engineering polymer is increased. In this case the engineering polymer does not contribute to char formation. Combinations of preceramic polymers and organic polymers can be envisioned in which the organic polymer component also combines, in a synergistic manner, with the preceramic component to enhance char formation. In example we refer to the Kraton™ w/ 20% PCS blend in Table 1. In this case the ceramic char from the preceramic polymers appears to increase the amount of carbonaceous char to produce a superior insulation barrier and decreases the amount of fuel for combustion in the gas phase.

Table 2. Physical properties for preceramic polymer-engineering polymer blends.

Material	Pk. Stress	Brk. Strain	Yng. Mod.	Melt Temp.	Char yld
PEBAX / PCS					
80/20	2313psi	7.0 in/in	1894 psi	118 C	18%
50/50	733	0.67	8333	125	44
30/70	1022	0.10	46830	216	56
20/80	—	—	—	200	69
PEBAX / PS					
80/20	2210	94	745	118	15
50/50	448	3.8	2253	110	43
30/70	280	5.9	5021	73	43
20/80	194	1.2	15530	52	50
PS	—	—	—	148	79
PCS	—	—	—	199	74
PEBAX	2778	82	617	119	20

PS = a polysilane copolymer containing  $(\text{PhSiMe})_{50}(\text{SiMe}_2)_{50}$ . Char yields determined by thermogravimetric analysis under nitrogen.

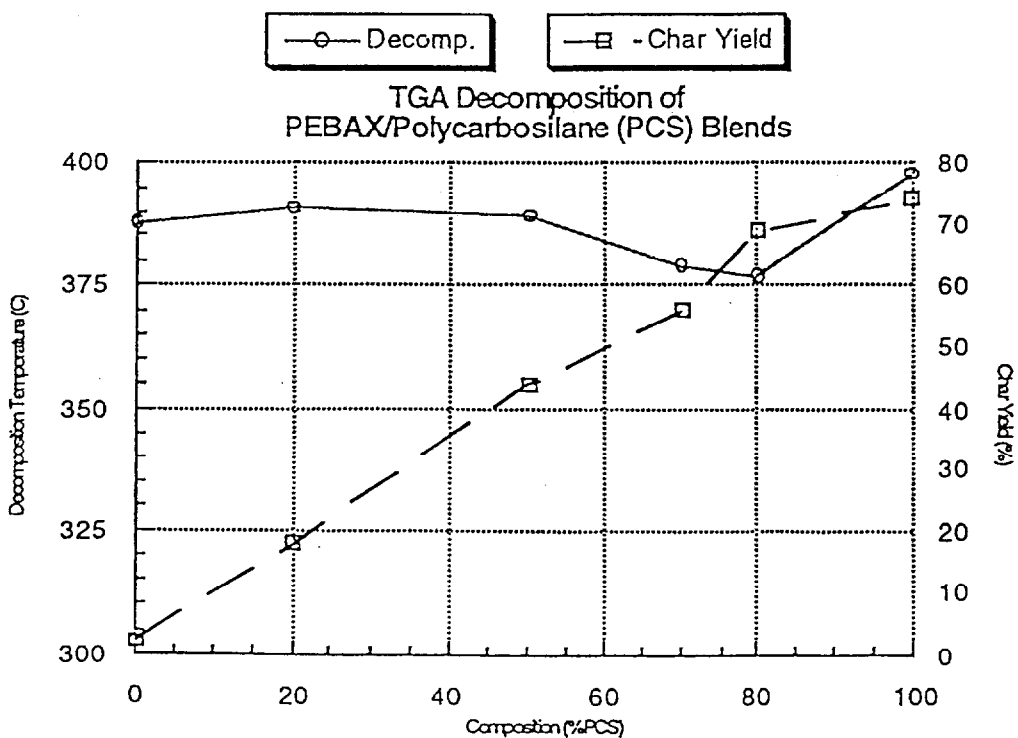


Fig. 4. Decomposition temperature and char yields for a preceramic polymer-engineering polymer blend.

### Example Process:

Blends of polycarbosilane (Dow Corning) or polysilastyrene (Hüls America) with PEBAX (Elf Atochem) or Kraton (Shell Chemical Co.) were prepared with preceramic weight fractions of 0.8, 0.7, 0.6, 0.5, and 0.2. Both components of the blend were weighed into a reactor followed by the addition of dichloromethane and tetrahydrofuran. The mixture was heated to the boiling point of the solvent while being mixed with a high shear emulsifier. The solution was poured into a Teflon mold and the solvent was evaporated for 24 hours at room temperature, then under vacuum at 80°C for 12 hours. The polymer blends were then hot pressed to make flat sheets for sample analysis. (Lichtenhan, Bolf) (Lichtenhan et. al U. S. Pat. 5,484,867)

Blend preparation without the use of solvents and swelling agents is also possible through the use of dispersive melt mixing equipment such as Bandbury™ mixers or twin screw extruders.

Note the process detailed here is not in anyway limited to the specific materials used or the processes described to prepare and enable them to function as FR plastics. For example FR preceramic polymer-polymer blends could be prepared using reactive processing techniques that enable or enhance the homogeneity (mutual compatibility and/or miscibility between the preceramic polymer and organic polymer). Likewise, non homogeneous preceramic polymer-polymer blends (mixtures of preceramic polymers and organic polymer showing incompatibility, immiscibility and phase separation) could be prepared and employed as effective FR plastics.

We claim the use of preceramic polymers as enabling components to be blended with common hydrocarbon-based plastics (organic polymers) and that these materials can function as FR plastics. The above example is provided so that those skilled in the art can implement the technology described in this disclosure.

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Per the preparation of blends with polyhedral oligomeric silsesquioxanes see: "Process for Preparation of Polyhedral Oligomeric Silsesquioxanes and Synthesis of Polymers Containing Polyhedral Oligomeric Silsesquioxane Group Segments" Lichtenhan, J. D.; Gilman, J. W.; Feher, F. J. U.S. Pat. 5,484,867 1996.